

Quantum Chemistry for Surface Segregation in Metal Alloys

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Objective

Metal alloys are vital materials for the fabrication of high-flux, high-selectivity hydrogen separation membranes. A phenomenon that occurs in alloys that does not arise in pure metals is surface segregation, where the composition of the surface differs from the bulk composition. Little is known about the strength of surface segregation in the alloys usually considered for hydrogen membranes. Despite this lack of knowledge, surface segregation may play a decisive role in the ability of appropriately chosen alloys to be resistant to chemical poisoning, since membrane poisoning is controlled by surface chemistry. The aim of this Phase I project is to develop quantum chemistry approaches to assess surface segregation in a prototypical hydrogen membrane alloy, fcc Pd₇₅Cu₂₅. This alloy is known experimentally to have favorable surface properties as a poison resistant H₂ purification membrane (Kamakoti et al., Science **307** (2005) 569-573), but previous efforts at modeling surfaces of this alloy have ignored the possible role of surface segregation (Alfonso et al., Surf. Sci. **546** (2003) 12-26).

Accomplishments to date

In performing quantum chemistry calculations for the surfaces of disordered alloys, a key challenge is to find an adequate tradeoff between performing calculations to sufficiently sample the configurations relevant to the surface and the time required to perform these calculations. We have focused on the (111) surface of fcc Pd₇₅Cu₂₅, as this is the most densely packed surface and will dominate the surface area of polycrystalline samples. We restricted our modeling of surface segregation to reordering of atoms within the top two layers of this surface by assuming that the third and deeper layers of the surface are substitutionally random. Density Functional Theory (DFT) calculations were performed using VASP with the PW91-GGA functional. All calculations used a computational supercell containing 4 (111) layers with the bottom two layers constrained in their bulk geometry and a (4x4) surface unit cell. Our calculations represent this surface in a vacuum. Extensions of this work to environments with appreciable pressures of H₂ and other gases is discussed below. A suite of more than 20 atomic configurations were examined, including configurations where the composition of the upper two layers was (i) equal to the bulk composition, (ii) representative of strong Cu segregation to the surface, that is, Pd₅₀Cu₅₀ in the top layer and pure Pd in the second layer, and (iii)

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representative of strong Cu anti-segregation from the surface, that is, pure Pd in the top layer and Pd₅₀Cu₅₀ in the second layer. For each set of layer compositions, a range of ordered and random distributions of the Pd and Cu atoms were explored. For each configuration, the surface layers were relaxed to minimize the configuration's total energy. A provocative conclusion from these initial calculations is that surfaces in which the top layer is pure Pd have significantly lower energies than the other configurations examined.

Our quantum chemistry calculations strictly only provide direct information on the energy of the surface at $T = 0$ K. Since we obviously need information on the state of the surface at finite temperatures, we have employed a cluster expansion approach (see, e.g., Blum and Zunger, Phys. Rev. B **72** (2005) 020104) to rigorously derive a lattice gas model that describes interactions between atoms. In conjunction with cluster expansions, we used the "Leave One Out" statistical approach to determine which interaction parameters are most significant. Screening a larger number of two and three body interactions in this way, we developed a lattice gas model for the energy of the upper two surface layers of a Pd₇₅Cu₂₅(111) surface. This description readily yields information at arbitrary temperatures when the equilibrium state of the lattice gas model is established via Kinetic Monte Carlo (KMC) simulations. Our KMC simulations show that strong anti-segregation of Cu out of the top surface layer occurs at the high temperatures relevant for coal gasification applications. At 700 °C, the surface is predicted to be more than 90 at.% Pd, and at lower temperatures the Pd content of this layer is even higher. This strongly suggests that earlier theoretical modeling of the surfaces of PdCu alloy membranes that neglected surface segregation may require revision.

Future work: We plan to perform calculations to probe the binding energy of atomic H on surfaces in which Cu is anti-segregated from the surface layer and will compare these binding energies to analogous results on substitutionally random surfaces. These binding energies are useful for correlating the properties of alloy surfaces with more general chemical properties (see, e.g., Greeley and Mavrikakis, Nature Materials **3** (2004) 810-815), in addition to being directly relevant to the performance of these surfaces as H₂ membranes. Analogous calculations for the binding energy of surface S will also be performed.

Papers and Presentations:

"First principles modeling of surface segregation in Pd-rich CuPd alloys", David S. Sholl, in preparation for *J. Molecular Catal. A*

"First principles methods for modeling Pd alloys as H₂ purification membranes", Preeti Kamakoti, Lymarie Semidey-Flecha, Sudhakar Alapati, and David S. Sholl, 135th TMS Annual Meeting, March 12-16, 2006, San Antonio, TX (invited presentation)

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